Chapter 1

INTRODUCTION

Corroles are tetrapyrrolic molecules, maintaining the skeletal structure of corrin, with its three meso carbon positions and one direct pyrrole-pyrrole linkage, and possessing the aromaticity of porphyrins (see figure 1.1). First reported by Johnson and Kay in 1965[1], corroles were the end product of a many step synthetic scheme, finally being formed by the photocyclization of a,c-biladienes. While this last step was simple, with 20-60% yields, the route to a,c-biladienes was far from easy. Indeed, the overall reaction from readily available starting materials to corrole was a multi-step synthesis, with poor yields in many of the reactions. Thus, while corroles have been known for more than 40 years, research in the field was slow to progress. It wasn't until the discovery of new synthetic methods for corroles developed in 1999 by different groups working independently that research in this area really started to expand[2].

This is not to say, however, that the field of corrole research was non-existent prior to the development of the new methodologies. While it was slow growing after the initial publication, it was far from stagnant, and many of the interesting properties of corroles were investigated by different groups. Among these properties is their ability to stabilize unusually high formal oxidation states of metal ions, such as iron(IV), cobalt(IV), and cobalt(V)[3, 4]. In fact, one particular corrole available through a method developed by Zeev

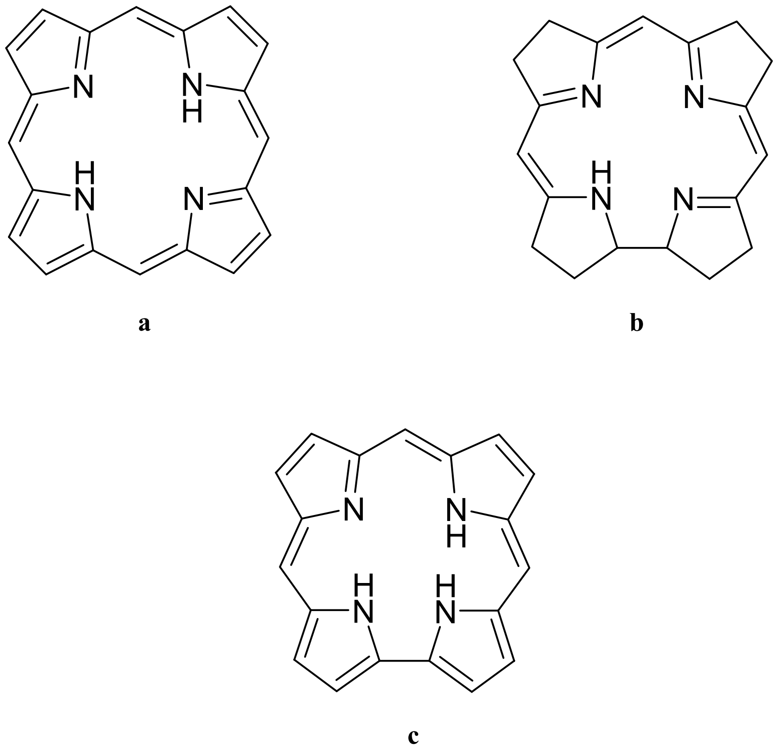

Figure 1.1. Skeletal structures of a) porphyrin, b) corrin, and c) corrole.

Gross, 5,10,15-tris(pentafluorophenyl)corrole, has been shown to stabilize four formal oxidation states of chromium, Cr(III, IV, V, IV)[5].

Now that the synthesis of corroles has been made easier, the field of corroles has greatly expanded. A quick search of the literature reveals that of all the papers published on corroles in the 40 years since Johnson and Kay's initial publication, almost three-quarters have come out in the last 5 years.

So what makes corroles so interesting? Aside from their ability to stabilize metal ions in higher oxidation states, corroles also possess many other very remarkable properties. Once synthesized, the ligands have shown themselves to be very versatile toward substitution and metallation reactions, allowing for numerous corroles with varying solubility properties, making them useful in many different applications. Some of these corroles form very tight conjugates with proteins, opening up possibilities for use in biological systems[6, 7].

Also among the interesting attributes of corroles are their photophysical properties. Corroles generally show porphyrin type spectra, with strong absorptions in the visible range associated with very highly colored compounds. As well, the direct pyrrole-pyrrole linkage seems to give corroles stronger fluorescence properties than their porphyrin counterparts[8]. These properties open up potential for using corroles in many other applications, including such diverse areas as cancer diagnosis and treatment, and solar cell research.

With all these different areas of research opening up to corroles, it is becoming clear that they are a very important class of molecules. And while their uses in other areas are interesting, it has also become clear that a fundamental understanding of the properties of these new molecules is needed. In many respects, corroles are very similar to porphyrins, possessing the same types of properties, but to varying degrees. This raises the questions of just why does the removal of one meso carbon cause these differences, and do these differences in fact make corroles better or worse than porphyrins in regard to applications to other systems? This work investigates the fundamental properties of corroles, in an attempt to determine just how this small change in the structure of the molecule can lead to the various properties seen in corroles, as well as to quantify these properties in selected cases.